Kinetic Studies on Removal of Fluoride from Drinking Water by using Tamarind Shell and Pipal leaf Powder

V. Ramanjaneyulu, M. Jaipal, Nookala Yasovardhan, S. Sharada*

Department of Chemical Engineering, JNTUACE, Anantapur-515002, (A.P.), India

Abstract

The study aimed to develop adsorbents from leaves of *Ficus religiosa* (Pipal) and *Tamarindus Indica* (Tamarind) fruit shell to remove fluoride from drinking water. Batch adsorption experiments were undertaken on natural adsorbents (*Tamarindus Indica* and *Ficus religiosa*) developed from locally available trees to assess their suitability to remove fluoride from drinking water. The effect of controlling parameters of adsorption like pH, dose of adsorbent, contact time and initial sorbate concentration on fluoride removal efficiency was studied and optimum values for maximum uptake were found. Tamarind fruit shell exhibited highest fluorine removal efficiency about 85% at pH of 2, initial fluorine concentration of 3 mg/l, contact time of 90 min, adsorbent dosage of 2g/100ml and maintaining temperature of 307 K. The maximum adsorption of fluoride for Pipal leaf powder (79%) was observed at pH 2, the optimum sorbent doses were found to be 2.0 g/l. The equilibrium was achieved in 1.5 and 2 hour, respectively. The obtained data were fitted to Langmuir and Freundlich isotherms.

Key words: Fluoride, Tamarind fruit shell, Pipal, Langmuir Isotherm, Freundlich Isotherm.

***Corresponding author: ph:** +919642853207

1. INTRODUCTION

Small amounts of fluorine are naturally present in water, air, plants and animals. Though a small concentration is beneficial for the maintenance of healthy bones and teeth, it is harmful when it exceeds the concentration more than 1.0mg/l. Fluorine that is located in soils may accumulate in plants. The amount of uptake by plants depends upon the type of plant and soil. Animals that eat fluorine containing plants may accumulate large amounts of fluorine in their bodies. Consequently, animals and humans that are exposed to high concentrations of fluorine suffer from dental decay and bone degradation. Finally, it can cause low birth-weights and also effects the growth in children[1].

Adsorption methods for fluoride removal by using several adsorbents such as bentonite, activated alumina, activated carbon, zeolites, charcoals and fly ash[2-8] have been studied to remove high fluoride concentrations. But these adsorbents were found to be expensive for treating fluoride bearing waters especially in rural areas and thus, recent attention of the world has been devoted to the study of natural, but effective low cost materials such as calcite, brick powder, fishbone charcoal, bagasse ash, thermally activated Neem, thermally activated kikar and activated kaolinites[9-14] have been studied for fluoride removal. However, due to lower efficiency or non-applicability on mass scale these techniques are not much in use. Adsorption potential of metal oxide (lanthanum, magnesium and manganese) incorporated bentonite clay was investigated for defluoridation of drinking water using batch equilibrium experiments to gain insight of adsorption behaviour, kinetics and mechanisms of adsorption of fluoride ion was studied by Priyadarshini Dixith et al[15].

In the present work, adsorbents were developed from Tamarind fruit shell and leaves of Ficus Religiosa (Pipal) to remove fluoride from water. The leaves of both the plants are amply available in India and are known for their medicinal and other purposes. Moreover, they have high fibre content making them suitable to be converted in biosorbents. Effect of various parameters like pH, dose of adsorbent, initial concentration of fluoride ion, and contact time was studied. A comparison of the adsorption efficiency of these adsorbent materials was done to determine which material is more suitable for removal of fluoride from drinking water. The experimental data was fitted into Langmuir and Freundlich isotherms.

2. MATERIALS AND METHODS

2.1. Adsorbent Preparation

The fresh leaves of Pipal and Tamarind fruit shell were taken and sun dried for 3 to 4 days in an open atmosphere and crushed manually. The raw materials were sieved with standard screen mesh no. 52/75, followed by chemical digestion using both acid and alkali treatment. The acid treatment incurred heating the leaf and Tamarind shell powder with 1N aqueous solution of HNO_3 for 20 min followed by washing with distilled water until the entire colour had been removed similarly, the alkali treatment involved heating the leaf and Tamarind shell powder with 1N aqueous solution of NaOH for 20 min, again followed by washing with distilled water until the entire colour had been removed. The adsorbent was dried to remove the moisture content.

2.2. Preparation of Adsorbate Solution

About 1.0 g of Sodium Fluoride salt was dissolved in 1.0 lit of distilled water and then the solution was diluted as required to obtain standard solutions containing 0.2, 0.4, 0.6, 0.8 and 1.0 g/l of fluoride.

2.3. Batch Adsorption Experiments

Batch Adsorption experiments were conducted by taking the known concentration of fluoride stock solution of 150 ml and known amount of adsorbent which is treated with acid and base was added to it. All the experiments were conducted at a room temperature 31 ± 2 ^{o}C, and pH was adjusted for 2.Then the mixture was agitated by using a mechanical agitator at a speed of 200 rpm for 60 min. The contents of the beakers were then allowed to settle for 2 minutes and the supernatants were carefully decanted and filtered through filter paper. The filtrate was collected and estimated for residual fluoride ion concentration by using a spectrophotometer.

$$\text{Removal of Flouride (\%)} = \frac{\text{Intial Flouride Concentration - Final Flouride Concentration}}{\text{Intial Flouride Concentration}} \times 100$$

Freundlich Isotherm

The linear Freundlich adsorption isotherm is given in Equation[16],

$$\log q_e = \log K_f + 1/n \log C_e$$

Where,

q_e is the amount of Adsorbate adsorbed per unit weight of adsorbents, mg /g,
C_e is the equilibrium Adsorbate concentration in solution, mg/l,
K_f and 1/n are the Freundlich constants.

Langmuir Isotherm

The Langmuir equation[17] is commonly written as, $q_e = abc_e / (1+bC_e)$

The linear form of Langmuir isotherm can be expressed as, $1/q_e = (1/a) + (1/abC_e)$

Where,

q_e The amount of solute adsorbed per gram of adsorbent (mg/g).

C_e The equilibrium Adsorbate concentration in solution, (mg/l).

a Number of moles of solute adsorbed per unit weight of adsorbent in forming monolayer on the surface.

b Constant related to energy.

3. RESULTS AND DISCUSSIONS

3.1. Percentage removal of fluoride with Tamarind fruit shell and Pipal leaves

Effect different parameters on removal of fluoride from drinking water by using Tamarind fruit shell and Pipal leaves are shown in Table1 and Table 2.

Table 1: Effect of Contact time and Adsorbent dosage on removal efficiency

Contact time (min)	Removal Efficiency, %		Adsorbent dosage, g/100 ml	Removal Efficiency, %	
	Tamarind	Pipal		Tamarind	Pipal
30	65	65	0.5	65	70
60	74	77	1.0	72	75
90	80	83	1.5	79	77
120	83	85	2.0	81	85
150	83	86	2.5	83	86

Table 2: Effect of pH and Initial fluoride concentration on removal efficiency

pH	Removal Efficiency, %		Initial fluoride Concentration (mg/l)	Removal Efficiency, %	
	Tamarind	Pipal		Tamarind	Pipal
2	85	79	3	82	79
4	78	70	5	80	61
6	70	55	10	75	56
8	55	46	15	51	45
10	46	42	20	46	38

3.2. Effect of Contact time

Contact time varied from 30 min to120 min and other parameters kept constant i.e. the test mixture containing adsorbent dose of 1g/100ml, initial fluoride ion concentration was 5mg/l and pH is 2 were adjusted to various contact times for both Tamarind fruit shell and Pipal. Observations were made at contact time of 30, 60, 90 and 120min respectively and these experiments were conducted separately for both absorbents at a room temperature 31±2 ^{o}C.

The effect of contact time using two adsorbents was compared in Fig 1. About 86% removal of fluoride was reported for Pipal leaves and 83%removal for Tamarind powder. It was observed that the removal of fluoride increases with increase with contact time for both adsorbents, but after sometime, it gradually approaches a constant value, denoting attainment of equilibrium. The fluoride removal increases from 65% to 86% in case of Pipal and 60% to 83% for Tamarind at 30 min and 150 min of contact time respectively.

3.3. Effect of Adsorbent Dose

The effect of adsorbent dosage varied from 0.5g/100ml to 2.5 g/100ml and other parameters kept constant i.e. the test mixture containing initial fluoride ion concentration was 5mg/l and pH is 2 were adjusted to various adsorbent dosages for both Tamarind fruit shell and Pipal. Observations were made at adsorbent dose of 0.5, 1.0, 1.5, 2.0 and 2.5 g/100ml and these experiments were conducted separately for both absorbents at a room temperature.

The percentage removal of fluoride increases with increase of adsorbent dosage for both adsorbents, but after sometime, it gradually approaches a constant value, denoting attainment of equilibrium. At pH 2 , initial fluoride ion concentration was fixed at 5 mg/l and contact time was kept as 90 min. Tamarind removes 65% of fluoride at a dose of 0.5 g/100ml which increases to 83% at 2.5 g/100ml and Pipal achieves 70% to 86% fluoride removal at doses of 0.5g/100ml to 2.5 g/100ml respectively at a room temperature.

3.4.Effect of pH

The effect of pH on removal of fluoride, test mixtures containing initial fluoride ion concentration is 5mg/l and 2 g/100ml of bio sorbent were adjusted to various pH values both in acidic and alkaline range, mixed for 60 min and analysed for residual fluoride ion concentration by a spectrophotometer. Observations were made at pH levels of 2, 4, 6, 8 and 10 and these experiments were conducted separately for both absorbents. The pH was maintained at desired value with ± 0.2 by adding 0.5 N HNO_3 or 0.1 N NaOH. The removal of fluoride ions decreases with increase in pH for both adsorbents. pH of 2, which gives maximum fluoride removal for both cases about 85 % for Tamarind shell and 79% for Pipal.

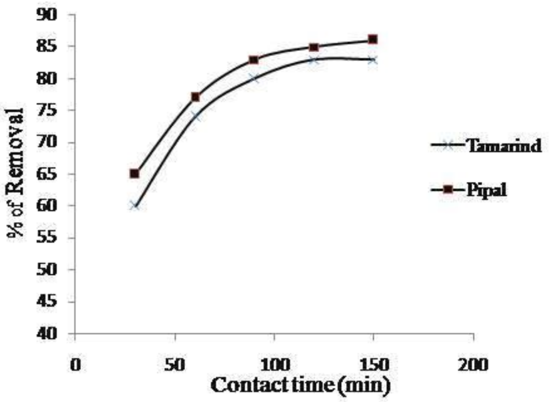

Fig.1. Effect of Contact time on % of removal

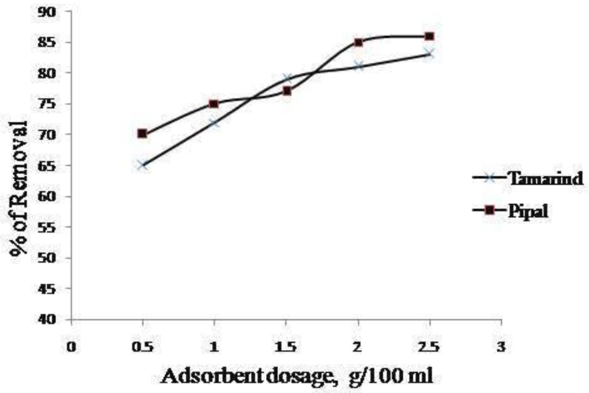

Fig.2. Effect of Adsorbent dosage on % of removal

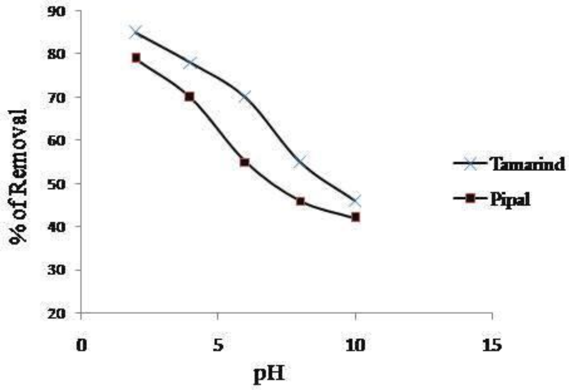

Fig.3. Effect of pH on % of removal

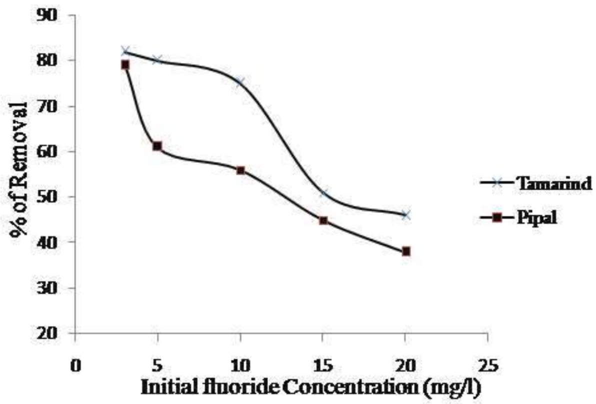

Fig.4. Effect of Adsorbent dosage on % of removal

3.5. Effect of Initial Fluoride Ion Concentration

The adsorbent dosage of 5 g/l and pH 2 was adjusted to various initial fluoride ion concentration ranges, mixed for 60 min and analysed for residual fluoride ion concentration by using spectrophotometer. Observations were made at Fluoride of 3, 5, 10 and 15 mg/l and these experiments were conducted separately for both absorbents. The effect of Initial fluoride ion concentration using two adsorbents was compared in the Fig 4 and was observed that the removal of fluoride ion decreases with increase in initial fluoride ion concentration. The percentage fluoride removal falls sharply from 79% to 38% for Pipal and 82% to 46% for tamarind shell when the concentration was increased from 3mg/l to 15 mg/l.

3.6. Adsorption Models

The experimental data were fitted to Freundlich and Langmuir isotherms and evaluated best fit model for this study.

Freundlich Isotherm

Freundlich isotherms were plotted between log q_e and log C_e as shown in the Fig 5 and Fig 6.

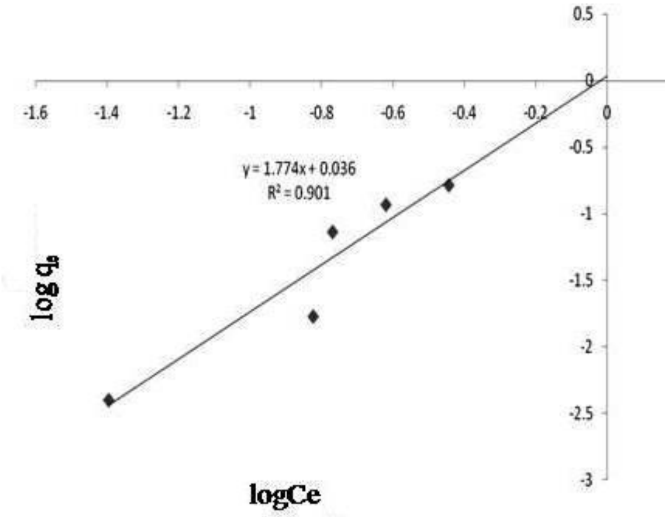

Fig.5: Freundlich Isotherm for Tamarind fruit shell

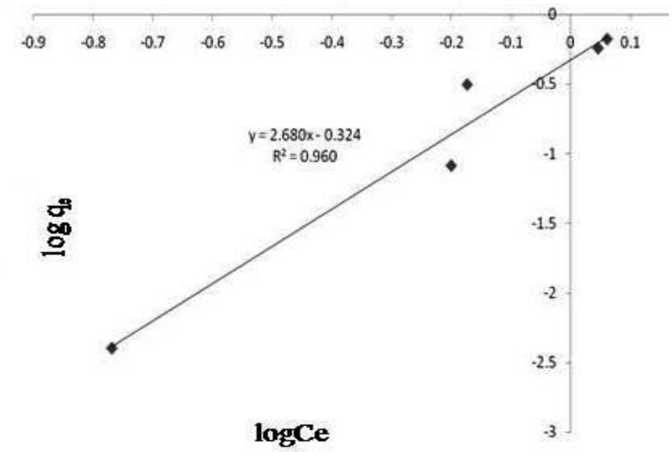

Fig.6: Freundlich Isotherm for Pipal leaves

Langmuir Isotherm

Langmuir isotherms in this study were plotted between $1/q_e$ and $1/C_e$ as shown in Fig.7 and Fig 8.

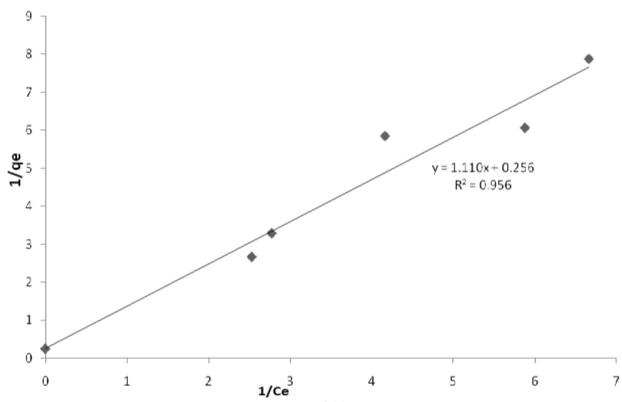

Fig. 7: Langmuir Isotherm for Tamarind fruit shell

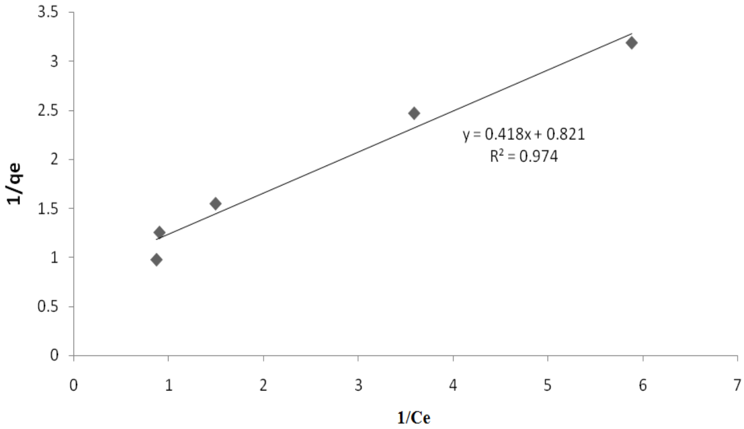

Fig 8: Langmuir Isotherm for Pipal leaves

From the adsorption isotherms plots, the kinetic constant for both the isotherms were evaluated for Tamarind fruit shell and Pipal leaves.

Table 3: Kinetic constants for bio sorbents

Adsorbent	K_f	1/n	a	b	Freundlich isotherm	Langmuir isotherm
Tamarind fruit shell	1.086	1.274	1.5384	1.352	$q_e=1.086C_e^{1.274}$	$(2.065\times C_e)/(1+1.352\times C_e)$
Pipal leaves	0.474	2.680	0.8000	2.189	$q_e=0.474C_e^{2.680}$	$(1.744\times C_e)/(1+2.189\times C_e)$

4. CONCLUSIONS

The utilization of waste material such as Pipal leaf powder and Tamarind fruit shell for the removal of fluorine from drinking water was investigated. The adsorbents used are natural, economically cheap and eco-friendly. The maximum adsorption of fluoride for tamarind fruit shell powder (85%) and Pipal leaf powder (79%) was observed at pH 2. From the experimental data the Langmuir isotherm was best fit since the correlation coefficients for Langmuir isotherm was higher than the Freundlich isotherm. With the increase of adsorbent amount the percentage removal of fluoride increases but the adsorption capacity decreases because of availability of more unsaturated adsorption sites. Tamarind fruit shell exhibited highest fluorine removal efficiency 85% at pH of 2, initial fluorine concentration of 3 mg/l, contact time of 90 min, adsorbent dosage of 2g/100ml and maintaining temperature of 307K. Fluorine removal for a given adsorbent increases with time, attaining equilibrium within 90 min. The maximum adsorption of fluoride for Pipal leaf powder (79%) was observed at pH 2, the optimum sorbent doses were found to be 2.0 g/l. The equilibrium was achieved in 1.5 and 2 hour, respectively. The Langmuir adsorption is found to be more suitable than Freundlich isotherm for both Tamarind fruit shell and Pipal.

REFERENCES

1. M.Ahmad, B.Ahmad, S.N. Hussain and S.mahmood, (2003) ‘Clinical investigations of skeletal fluorosis in children of manga Mandi in pakistan’, Pakistan Journal of Pharmacetical Science, Vol.16, 2, 9-10.
2. M. Srimurli, Pragathi A, Karthikeyan J. (1998). A Study on Removal of Fluorides from Drinking Water by Adsorption onto Low Cost Materials. Jour. Environmental Pollution, vol 99, 285.
3. W W Choi and K Y Chen. (1979) 'The Removal of Fluoride from Waters by Adsorption'. Journal of AWWA, vol 71, 10, 562.
4. Y C Wu and ANitya.(1979) 'Water Defluoridation with Activated Alumina'. Journal of Environmental Engineering, 357.
5. Y H Li, et al. (2001) 'Adsorption of Fluoride from Water by Amorphous Alumina Supported on Carbon Nanotubes'. Journal of Chem. Phys. Lett., vol 350, 412.
6. W S Jhonston and R H McKee. (1934) 'Removal of Fluoride from Drinking Water'. Journal of Industrial Engineering Chemistry, vol 26, no 8, 849.
7. D S Bhargava and D J Killedar. (1992) 'Fluoride Adsorption on Fishbone Charcoal through a Moving Media Adsorption Column'. Water Research, vol 26, 781.
8. A VJamode, V S Sapkal, V S Jamode and S K Deshmukh. (2004) 'Adsorption Kinetics of Defluoridation using Low Cost Adsorbents'. Journal of Adsorption Science and Technology, vol 22, no 1, (b), 65.
9. M Yang. (1999) Fluoride Removal in A Fixed Bed Packed with GranularCalcite.Water Research, vol 33, 16, 3395.
10. R Piekos and S Paslawska. (1999) 'Fluoride Uptake Characteristics of Fly Ash'.International Society for Fluoride Research, vol 32, no 1, p 14.
11. A V Jamode, V S Sapkal and V S Jamode. (2004a) 'Defluoridation of Water using Inexpensive Adsorbents'. J. Indian Institute of Science, vol 84, 163-171.

12. D S Bhargava and D J Killedar. (1993) 'Effect of Stirring Rate and Temperature on Fluoride Removal by Fishbone Charcoal'.Indian Journal of Environmental Health, vol 35, no 2, p 81.
13. Sunil Kumar, Asha Gupta and J.P. Yadav (2008) Removal of fluoride by thermally activated carbon prepared from neem (Azadirachtaindica) and kikar (Acacia arabica) leaves Journal of Environmental Biology volume 136, pages 227 232.
14. S. Meenakshi, C. SairamSundaram and Rugmini Sukumar (2008) Enhanced fluoride sorption by mechano chemically activated kaolinites, Journal of Hazardous Materials Volume 153, Issues 1-2, 164-172.
15. Sanjay P.Kamblea, Priyadarshini Dixith Sadhana S. Rayalu and Nitin K. Labhsetwarb (2009) Defluoridation of drinking water using chemically modified bentonite clay Desalination, Volume 249, Issue 2, 687-693.
16. H Freundlich. (1907) uber die adsorption in losungen. Z.phys.Chem. 57, 385-470.
17. I Langmuir. (1916) The constitution and fundamental properties of solids and liquids, I.Solids, J.am.Chem.Soc. 38, 2221-2295.